Microstructural properties of $(Ba,Sr)TiO_3$ films fabricated from $BaF_2/SrF_2/TiO_2$ amorphous multilayers using the combinatorial precursor method

I. Takeuchi,[a] K. Chang, and R. P. Sharma
Small Smart Systems Center, Department of Materials Science and Engineering and Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742-2115

L. A. Bendersky
National Institute of Standards and Technology, Gaithersburg, Maryland

H. Chang, X.-D. Xiang, E. A. Stach, and C.-Y. Song
Lawrence Berkeley National Laboratory, Berkeley, California

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We have investigated the microstructure of $(Ba,Sr)TiO_3$ films fabricated from $BaF_2/SrF_2/TiO_2$ amorphous multilayers. Rutherford backscattering spectroscopy and x-ray diffraction studies show that a controlled thermal treatment can interdiffuse the multilayers so as to create predominantly single-phase epitaxial $(Ba,Sr)TiO_3$ films. A high resolution cross-sectional transmission electron microscopy investigation of the processed films shows that they consist of large epitaxial grains of $(Ba,Sr)TiO_3$ with atomically sharp interfaces with the $LaAlO_3$ substrates. In addition, we have identified regions where polycrystalline and transient phases exist in small pockets in the film matrix. The results here indicate that the combinatorial thin-film synthesis using precursors can produce $(Ba,Sr)TiO_3$ films in combinatorial libraries which exhibit properties similar to those films made by conventional techniques. © *2001 American Institute of Physics.*
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INTRODUCTION

Combinatorial thin-film materials synthesis has proven to be a powerful tool in exploring new and improved compositions of electronic materials.[1–6] Its utility and effectiveness have been demonstrated with high T_c superconductors and in successful discoveries of a novel phase of magnetoresistive materials and a series of new luminescent materials. Recently, it has also been used to improve and optimize properties of ferroelectric/dielectric materials.[3,4–6] There are several different methods of creating large compositional variation in thin-film combinatorial libraries and composition spreads. One such fabrication method, the precursor method, can truly bring out the combinatorial nature of the synthesis approach because it creates different compositions from multilayers of amorphous precursors. By varying the combinations and thicknesses of precursors deposited at different positions, one can generate very diverse compositional variation across the libraries. In this method, following the depositions, libraries undergo controlled thermal treatments to (1) diffuse and mix the precursors and (2) crystallize appropriate compounds at each site. We have demonstrated by x-ray diffraction that this technique can be used to obtain predominantly single-phase epitaxial films on lattice-matched substrates.[3,6]

$(Ba,Sr)TiO_3$ (BST) with a perovskite structure represents a very important materials system whose applications are widely pursued for use in a variety of fields. Properties of ceramic BST have been studied for decades. We have previously fabricated various thin-film libraries of BST and related compounds in search of improved ferroelectric/dielectric materials for thin-film microwave device and dynamic random access memory (DRAM) applications. From the dopant libraries, we have found that W doped BST exhibits lower leakage current and lower microwave loss compared to undoped BST.[3,4] $Ba_{0.12-0.25}Sr_{0.35-0.47}Ca_{0.32-0.53}TiO_3$ was identified from a continuous composition spread of $(Ba,Sr,Ca)TiO_3$ as a compositional region with relatively low microwave loss.[6] In these experiments, the desired composition at each position of the library was created by combining different ratios of BaF_2 or $BaCO_3$, SrF_2 or $SrCO_3$, and TiO_2. The amorphous layers were deposited on (100) $LaAlO_3$ (LAO) by sputtering and/or pulsed laser deposition. Carefully controlled thermal treatments of the precursor multilayers resulted in the formation of predominantly epitaxial BST films at each site.

Although this technique is far from conventional for fabricating BST films, the same precursors and similar postannealing processes are commonly used in fabricating bulk ceramic BST. BaF_2 have also been used in fabrication of early $YBa_2Cu_3O_{7-x}$ films, where Y, BaF_2, and Cu were coevaporated onto room temperature substrates, and subsequently annealed in oxygen for formation of the

[a]Electronic mail: takeuchi@squid.umd.edu

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compound.[7,8] In these studies, it was observed that temperatures above 800 °C were required for complete dissociation of BaF_2 and successful formation of $YBa_2Cu_3O_{7-x}$. Successful thin-film fabrication from precursors has been demonstrated in many metal–oxide systems.[1–3,5,6] There are other nonoxide materials systems whose novel phase spaces may also be pursued with the combinatorial synthesis using precursors. For instance, high quality thin films of I–III–VI semiconductors such as chalcopyrites $CuInSe_2$ have been successfully fabricated by seleniding and/or sulfiding annealed multilayers of metal and/or metal–oxide precursors.[9] This suggests that these materials systems can perhaps also be explored through a combinatorial approach using a similar fabrication technique. However, the precursor technique is not universally applicable to all materials systems. Even when the predominantly formed phase is the desired phase, other minority phases and regions with microstructural deviations are expected to occur.

The success and integrity of the combinatorial thin-film approach using the precursor technique depends on how well one can map out the trend with which the compositional variation changes the physical properties across the library. This does not usually translate to having to fabricate materials with absolutely no minority phases and microstructural defects within each compositional region. For instance, in superconductor libraries, as long as there is a sizable superconducting domain within a fixed (by design) compositional region, most measurement techniques can detect their presence. On the other hand, there are materials properties that are critically affected by small amounts of impurity phases and defects. Applicability of the precursor technique to a specific materials system needs to be determined on a case-by-case basis, and its success depends on the degree to which defects can affect the macroscopic physical property of interest.

In order to investigate the limit of the precursor technique for making libraries of various materials, it is important to understand the details of the phase formation process and microstructural development in thin films made from precursors. To this end we have performed high resolution cross-sectional transmission electron microscopy (TEM) on BST films made from precursors. In particular, we have looked at films made with fluoride precursors. Such studies can also help elucidate the fundamentals of crystal formation process in BST. We find that there are indeed large epitaxial grains with atomically sharp interfaces with the substrate. Along with these grains, polycrystalline regions are also found.

EXPERIMENT

The precursor films studied here were deposited by pulsed laser deposition and/or sputtering onto (100) LAO substrates at room temperature. Some samples were also deposited on (100) MgO for Rutherford backscattering spectroscopy study. The TiO_2 layer is deposited first, followed by the deposition of $(Ba, Sr)F_2$. The required thicknesses of the layers to be deposited were calculated based on the density and the molecular weight of the precursors. For instance, ≈130 nm of BaF_2 and ≈70 nm of TiO_2 were used to obtain ≈200 nm of $BaTiO_3$. We have found that the change in the total film thickness after the annealing processes is negligible. Following the deposition, the samples were placed in a 200 °C oven for a week. This turned out to be a crucial step in the annealing process: When this period is not long enough, subsequent annealing does not lead to proper crystalline compound formation.[10] Following the 200 °C anneal, the samples were annealed at 900 °C for 1.5 h in flowing O_2. Some of the samples were also annealed at 400 °C for 24 h prior to the 900 °C anneal. However, this additional annealing step at 400 °C resulted in no substantial differences in microstructure. All furnace ramp rates were 1 °C/min. This annealing procedure is identical to the one used in processing combinatorial libraries of BST and related materials in our prior work.[3,6] For the present study, typically a set of samples were placed in the furnace to be annealed together and were taken out one after another successively at different temperatures, so that we could observe the evolution of the diffusion process as well as phase formation.

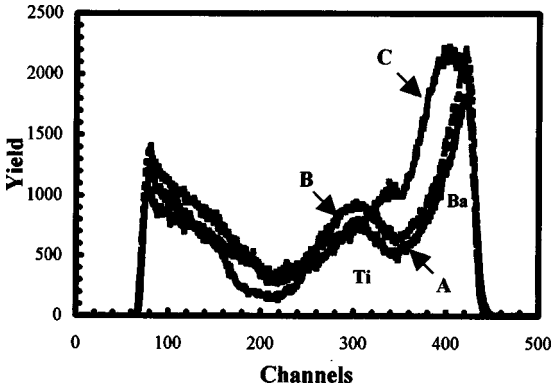

FIG. 1. RBS spectra of BaF_2 (130 nm)/TiO_2 (70 nm) on (100) MgO annealed in flowing oxygen as the temperature was ramped up at 1 °C/min. Samples A, B, and C were annealed up to 400, 700, and 900 °C, respectively.

RESULTS AND DISCUSSION

Rutherford backscattering spectroscopy (RBS) and x-ray diffraction were utilized extensively to characterize the processed thin films. Figure 1 shows a series of RBS spectra for BaF_2/TiO_2 samples which were taken out at various stages in the annealing process. These particular samples were made on (100) MgO substrates so that Ba and Ti peaks are clearly visible in the RBS spectra. In general, the peaks are significantly broader compared to what one expects from such multilayers. This is due to the marked roughness (on the order of 100 nm) of the BaF_2 precursor layer which occurs at a lateral length scale much smaller than the beam spot size of He beam (≈400 μm) used for RBS. Thus, rather than fitting the spectra for quantitative analysis, we discuss the qualitative results. As the samples experienced a continuous increase in annealing temperatures from 400 °C (curve A) to 700 °C (curve B), the peaks appeared to have become slightly broadened indicating that there was small amount of diffusion that had taken place in between 400 °C and 700 °C. In contrast, the sample taken out at 900 °C (curve C) displays

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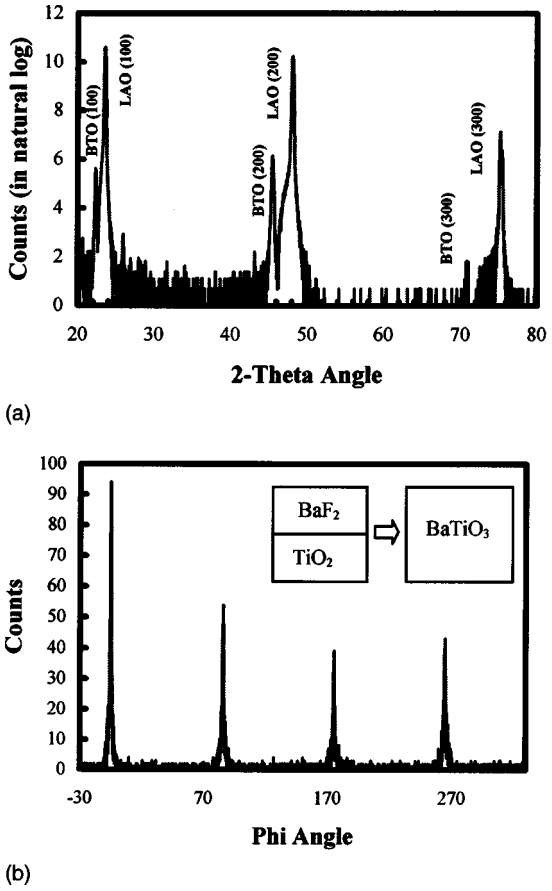

FIG. 2. (a) θ–2θ scan of BaF_2 (130 nm)/TiO_2 (70 nm) on (100) $LaAlO_3$ annealed up to 900 °C. Strong peaks from (100) $BaTiO_3$ are observed. (b) ϕ scan of the (101) plane of the same film. The inset shows a schematic of the phase formation process from precursors.

a substantial change in the spectrum indicating that significant diffusion had taken place between 700 °C and 900 °C.

The phase formation process is found to occur concomitantly with the diffusion process. x-ray diffraction was used to characterize the crystallinity of the annealed samples. In all cases in which the samples were annealed at up to temperatures $<700\,°C$, there were no visible peaks from the films. In contrast, samples taken out at 900 °C showed clear peaks from $(Ba, Sr)TiO_3$ indicating that most of the phase formation occurred between these temperatures. Figure 2 shows the x-ray diffraction results from one such BaF_2/TiO_2

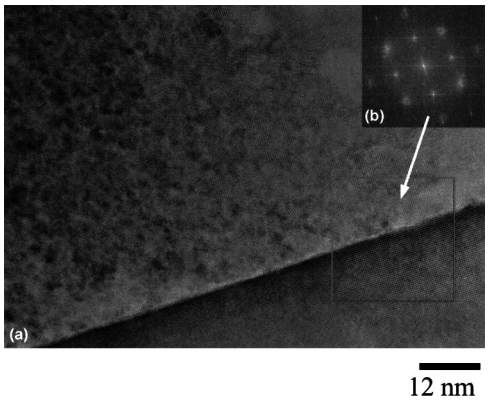

FIG. 3. (a) Cross-sectional HRTEM of $Ba_{0.5}Sr_{0.5}TiO_3$ made from precursors on $LaAlO_3$. The image is taken along the [010] direction. A large epitaxial grain with an atomically sharp interface is observed. (b) Computed diffractogram from a selected region in (a).

sample on (100) LAO annealed and taken out of the furnace at 900 °C. The θ–2θ scan [Fig. 2(a)] clearly shows the peaks from the (100) oriented $BaTiO_3$. As seen in this logarithmic plot, no other discernible phases are present in the film. The full width at half maximum (FWHM) of the (200) peak is 0.35°, which compares with 0.3° for the FWHM of the same peak of a typical $BaTiO_3$ film on LAO *in situ* deposited (onto a heated substrate) by pulsed laser deposition.[11] The peak broadening is an indication of the presence of defects and the nonideal crystallinity in the films made from precursors. Figure 2(b) is a ϕ scan of the (101) plane of $BaTiO_3$ of the same film. The fourfold symmetry indicates epitaxial growth of the film on (100). LAO with the expected cube-on-cube relationship. The FWHMs of the peaks are 1°, which is the same as those from typical *in situ* grown films indicating good in-plane orientation. Similar numbers have been obtained in other $(Ba, Sr)TiO_3$ films made from precursors.[10]

Figure 3(a) is a cross-sectional high-resolution transmission electron microscopy (HRTEM) image of a $Ba_{0.5}Sr_{0.5}TiO_3$ film made from precursors on (100) LAO. The image is taken along the [010] direction. A large continuous epitaxial grain is seen. Figure 3(b) is a computed diffractogram from a selected region in Fig. 3(a), and it attests to the cube-on-cube epitaxial relationship. Figure 4(a) is a HRTEM image of a $(Ba_{0.8}Sr_{0.2})TiO_3$ film made from precursors taken at higher magnification. The selected area diffraction (SAD)

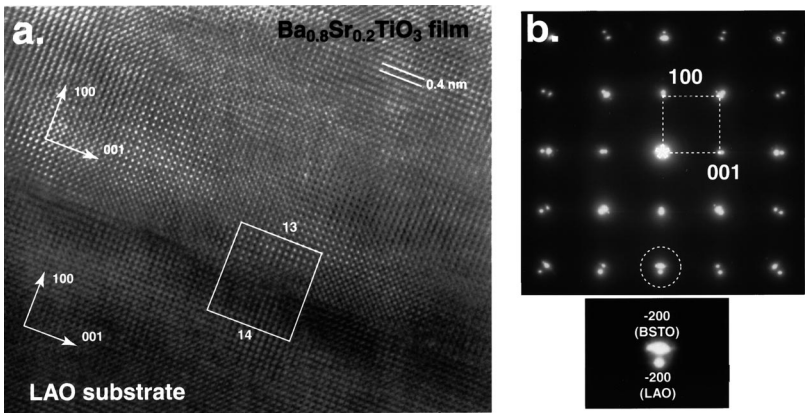

FIG. 4. $Ba_{0.8}Sr_{0.2}TiO_3$ film made from precursors on $LaAlO_3$. The image is taken along the [010] direction. (a) HRTEM image showing an epitaxial relationship between the substrate and the film. A Burgers circuit shows the presence of an interfacial misfit dislocation. (b) Corresponding selected area diffraction of both the substrate and film showing a cube-on-cube orientation relationship. An enlargement of (200) reflections shows a spread of orientations for the $Ba_{0.8}Sr_{0.2}TiO_3$ film.

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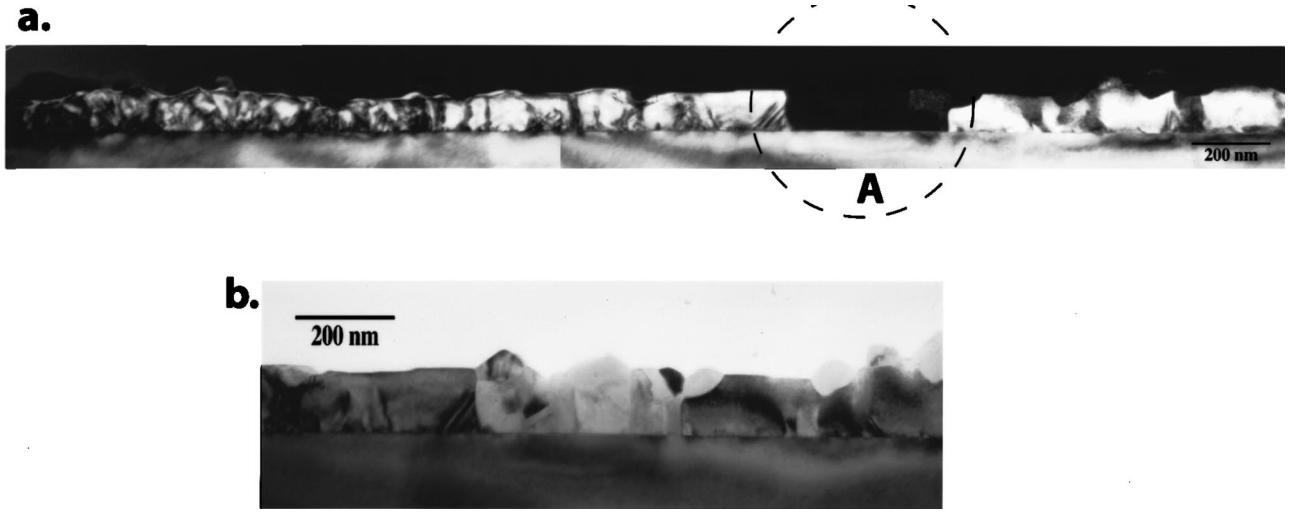

FIG. 5. (a) Low magnification cross-sectional dark field image of a $BaTiO_3$ film made from precursors. The image was taken with both $LaAlO_3$ and $BaTiO_3$ (010) reflections, and its bright contrast represents a cube-on-cube oriented continuous epitaxial film. The continuity of the film is interrupted in the region marked A. (b) Bright field image of that region. A selected area diffraction of this region shows the presence of polycrystalline grains with structures different from that of $BaTiO_3$.

pattern [Fig. 4(b)] indicates that the film has a (100) orientation, and it has a cube-on-cube epitaxial relationship with the substrate. A Burgers circuit shows the presence of a **b** $=[001]a$ interfacial misfit dislocation. At the bottom of Fig. 4(b) is an enlargement of (200) reflections, which shows a spread of orientations for the $(Ba_{0.8}Sr_{0.2})TiO_3$ film. It is from the mosaic spread associated with the formation of misfit dislocations. The film has an atomically sharp interface with the substrate. The period of dislocation is $\approx$20 unit cells, which is consistent with the lattice mismatch between LAO and the c axis of $(Ba_{0.8}Sr_{0.2})TiO_3$. Images such as these clearly indicate that the film growth nucleated at the interfaces.

Along with the epitaxial grains, which are the dominant feature of the films, we also encountered regions that displayed the formation of polycrystalline grains. The overall volume fraction of these regions is such that they do not appear in the standard large area powder-type x-ray diffraction, which only displays peaks from the large epitaxial grains [Fig. 2(a)]. Figure 5 is a low magnification cross-sectional dark field image of a $BaTiO_3$ film made from precursors. The image was taken along the [010] direction. It was taken with both LAO and BTO (010) reflections, which are very close to each other. Its bright contrast represents a substrate and BTO regions which are in cube-on-cube orientation. The continuity of the epitaxial film is interrupted in the region marked A. Figure 5(b) is a bright field image of region A. The image and SAD diffraction (not shown here) of this region indicate the presence of polycrystalline grains with structures different from that of $BaTiO_3$. The extent of the distribution of these regions in the film depends on the deposition/annealing conditions, and it varies somewhat from sample to sample, but all the samples we have studied exhibited areas with such nonepitaxial regions. Although the exact mechanism is not clear, in this particular case, we believe it was the nonuniformity in the thickness of the deposited BaF_2 in the region which led to the formation of the polycrystalline region. Polycrystalline grains in such regions have most likely nucleated inside the bulk of the film, rather than at the interface.

We have also observed the occurrence of microstructural defects at a much smaller scale. Figure 6 is a high-resolution image taken of a $Ba_{0.8}Sr_{0.2}TiO_3$ sample. The image is taken along the [010] direction, and the image region is 150 nm wide. Here, there are polycrystalline phases at the interface, and above them (above the dotted line), there is an epitaxial grain, which had apparently nucleated at a nearby interface region and continued to grow over the nonepitaxial region shown. For the most part, individual nonepitaxial domains such as these are small (at most tens of nm in size), and they have likely formed as a result of nonuniform diffusion of the precursors. Different regions marked by letters of the alphabet are identified as epitaxial and oriented cube on cube (a, b, and c), nonepitaxial perovskite (d), Ba–Sr–Ti–O transient

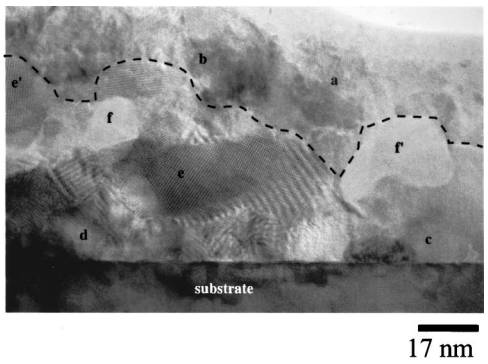

FIG. 6. Cross-sectional HRTEM of a $Ba_{0.8}Sr_{0.2}TiO_3$ film made from precursors on $LaAlO_3$. The image is 150 nm across, and it was taken along the [010] direction of the substrate. Regions a, b, and c are epitaxial and are oriented cube on cube with the substrate. Region d is epitaxial but textured. Regions e and e′ are transient phases. Regions f and f′ are grains in orientations that do not form lattice fringes. The dotted line is the boundary between epitaxial and nonepitaxial regions.

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phases (e and e′), and grains in orientations not forming lattice fringes (f and f′). The transient phases have formed as a result of incomplete interdiffusion of the precursors, and their crystal structures are different from that of the perovskite phase. An example of a transient phase is $BaTi_2O_5$. The formation of these phases is dictated by the local equilibrium of off-stoichiometric composition distribution. Since the precursor diffusion and the BST crystallization take place at right around the same temperature range (700–900 °C), it is likely that such phases form prematurely in some localized regions prior to completion of uniform interdiffusion. There is evidence that the some of the transient phases eventually turn into the correct perovskite BST phases upon further annealing. We are currently investigating the nature of this process.[12]

The dielectric properties of the films were measured using interdigitated electrodes at 1 MHz and a scanning evanescent microwave microscope at 1 GHz.[13] The precursor films have been shown to display complex dielectric constants in the same range as the ones measured from *in situ* grown films of the same compositions *in situ* deposited on heated substrates.[10] In particular, for a 200 nm thick $BaTiO_3$ film, ϵ and tan δ were 840 and 0.094 at 1 MHz and 590 and 0.42 at 1 GHz, respectively, measured at room temperature.

CONCLUSION

We have studied the microstructural details of $(Ba, Sr)TiO_3$ films made by annealing $BaF_2/SrF_2/TiO_2$ amorphous multilayers in flowing oxygen. We have found that predominant interdiffusion of the precursor layers as well as phase formation take place at $\geqslant$700 °C. High-resolution cross-sectional TEM of the films reveals that a large fraction of the films consists of epitaxial regions. This confirms the validity of the combinatorial technique as applied to this materials system, and the films obtained in combinatorial libraries made from precursors can be expected to display properties similar to those made by more conventional techniques. Further investigation of the phase nucleation and its evolution in annealed precursor films is currently under way.

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